PB90-116963

Application of High Performance Liquid Chromatography/Mass Spectrometry to Environmental Analysis

(U.S.) Environmental Monitoring Systems Lab., Las Vegas, NV

Oct 89

U.S. Department of Commerce
National Technical Information Service
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TECHNICAL REPORT DATA
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1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA/600/4-89/033		PB90 116963/AS

4. TITLE AND SUBTITLE
THE APPLICATION OF HIGH PERFORMANCE LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY TO ENVIRONMENTAL ANALYSIS

5. REPORT DATE
October 1989

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
L.D. Betowski and T.L. Jones

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
P.O. Box 93478
Las Vegas, NV 89193-3478

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS
U.S. Environmental Protection Agency
Envrionmental Monitoring Systems Laboratory
P.O. Box 93478
Las Vegas, NV 89193-3478

13. TYPE OF REPORT AND PERIOD COVERED
Project Report 10/1/88-5/31/89

14. SPONSORING AGENCY CODE
EPA/600/07

15. SUPPLEMENTARY NOTES

16. ABSTRACT

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Two different sets of compounds were used in this study. Organic dyes were used to test the improvements in the system. Since work was performed with dyes previously and since dye compounds encompass a variety of structural functionalities, the dyes made good test compounds. Chlorinated herbicides were studied in an effort to analyze for these compounds directly without having to prepare derivatives before separation.

This report covers a period from October 1, 1988, to May 31, 1989, and work was completed as of July 31, 1989.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	47
	20. SECURITY CLASS (This page)	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

PB90-116963

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by

L. D. Betowski and T. L. Jones
Quality Assurance and Methods Development Division
Environmental Monitoring Systems Laboratory
Las Vegas, Nevada 89193-3478

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
LAS VEGAS, NEVADA 89193-3478

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NATIONAL TECHNICAL INFORMATION SERVICE
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CONTENTS

Abstract iii

Figures vi

Tables vii

Abbreviations and Symbols. viii

Acknowledgment x

1. Introduction 1

2. Conclusions. 4

3. Recommendations. 6

4. Experimental Procedures. 7
   - General Procedures. 7
     - Thermospray Ionization HPLC/MS and HPLC/MS/MS . . . 7
     - Particle Beam HPLC/MS 10
   - Materials 10

5. Results and Discussion 18
   - Dyes. 18
   - Chlorinated Herbicides 24

References 36

FIGURES

Number		Page
1.	Schematic diagram of thermospray ion source with wire-repeller (sensitivity enhancement configuration)	8
2.	Schematic diagram of thermospray ion source with wire-repeller (repeller induced dissociation configuration)	9
3.	Particle beam HPLC/MS adapter. Heater wires are placed in drilled holes along the axis in the Vespel	11
4.	Structures of dyes	12
5.	Structures of herbicides	15
6.	Reconstructed ion current traces of ions at $^{m}/_{z}$ 297 and $^{m}/_{z}$ 267, and the total reconstructed ion current, following four successive injections of 50 pg of Disperse Blue 3.	20
7.	EI mass spectrum of Basic Green 4.	25
8.	CAD spectrum of the ion at $^{m}/_{z}$ 126 in Basic Green 4	26
9.	MS/MS spectrum of 2,4-DB.	31
10.	Repeller-induced CAD spectrum of 2,4-D.	32
11.	Repeller-induced CAD Spectrum of 2,4-DB	33

TABLES

1. Detection Limits For Commercial Dyes 19

2. Thermospray Ionization Positive Ion Spectra Of Sulfonated Azo Dyes 22

3. Particle Beam EI Mass Spectra of Azo Dyes 23

4. CAD Spectra of $(M+H)^+$ Ions of Azo Dyes Generated by Thermospray Ionization 24

5. Thermospray Ionization Repeller-induced CAD Mass Spectra of Azo Dyes 27

6. Positive Ion Thermospray Mass Spectra of Chlorinated Acid Herbicides 27

7. Limits of Detection in the Positive and Negative Ion Modes for the Chlorinated Acid Herbicides 28

8. Negative Ion Mass Spectra of Chlorinated Acid Herbicides (Discharge On) 30

9. Positive Ion Thermospray Repeller-induced CAD Spectra of Chlorinated Acid Herbicides 34

10. Comparison of Method Detection Limits: Method 8150 vs. Thermospray HPLC/MS 35

ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

A	--	ampere
atm	--	atmosphere
°C	--	degrees centigrade
CAD	--	collision activated dissociation
CI	--	chemical ionization
C.I.	--	Colour Index
cm	--	centimeter
2,4-D	--	(2,4-dichlorophenoxy)-acetic acid
2,4-DB	--	4-(2,4-dichlorophenoxy)-butanoic acid
DLI	--	direct liquid introduction
EI	--	electron impact
FSCC	--	fused silica capillary column
GC	--	gas chromatography
HPLC	--	high performance liquid chromatography
LOD	--	limit of detection
M	--	molar
mA	--	milliampere
MAGIC-LC/MS	--	monodisperse aerosol generation interface for combining liquid chromatography with mass spectrometry
MCPA	--	(4-chloro-2-methylphenoxy)-acetic acid
MCPP	--	2-(4-chloro-2-methylphenoxy)-propanoic acid
MDL	--	method detection limit
min	--	minute
mL	--	milliliter
mm	--	millimeter
MS	--	mass spectrometry
MS/MS	--	tandem mass spectrometry
mTorr	--	milliTorricelli
$^{m}/_{z}$	--	mass-to-charge ratio
µg	--	microgram
µL	--	microliter
µm	--	micrometer (micron)
ng	--	nanogram
PMN	--	Pre Manufacturing Notice
sec	--	second
SW-846	--	Test Methods for Evaluating Solid Wastes
T	--	temperature
2,4,5-T	--	(2,4,5-trichlorophenoxy)-acetic acid
Torr	--	Torricelli
2,4,5-TP	--	2-(2,4,5-trichlorophenoxy)-propionic acid (Silvex)
V	--	volts

SYMBOLS

C	--	carbon
Cl	--	chlorine
H	--	hydrogen
M^+	--	molecular ion
N	--	nitrogen
Na	--	sodium
O	--	oxygen
S	--	sulfur
X^-	--	anion

ACKNOWLEDGMENT

The authors wish to acknowledge the great assistance of Dr. Jehuda Yinon, who was an EPA Visiting Scientist in our laboratory from October 1988, to April 1989. We also acknowledge the peer review comments of Dr. Dennis Miller of Lockheed ESC and Dr. Ross Willoughby of EXTREL Corp.

SECTION 1

INTRODUCTION

The quest for the interfacing of high performance liquid chromatography (HPLC) to mass spectrometry (MS) has been actively pursued for at least 10 years. The goal of this search has been to make the combination of HPLC/MS as convenient and reliable as gas chromatography/mass spectrometry (GC/MS). The current use of GC/MS is characterized by its simplicity, the resolution of chromatographic peaks (with fused silica capillary columns [FSCC]), the reproducibility of both chromatograms and spectra, and the ease of quantification. The glass jet separator and now the FSCC directly interfaced to the mass spectrometer have been some of the technological advances that have contributed to the standing that GC/MS has achieved as the primary instrumentation in environmental analysis.

The reason for the increased interest in HPLC was that the GC-based technologies were limited in their scope of compounds that could be analyzed. For reasons of nonvolatility, thermal lability or intractability, an estimated 80 percent of organic compounds are not amenable to or are difficult to analyze by GC methods.

The operation of interfacing an HPLC to a mass spectrometer offers many more problems than the similar fusion of GC to MS. The HPLC operates at high flows (1–2 mL/min) of a liquid at high pressure (70–150 atm) while the pressure regime of the mass spectrometer is approximately 10^{-9} atm. Normally, the flow of the HPLC would overwhelm the vacuum system of the mass spectrometer. Two of the initial applications of interfacing the HPLC to the mass spectrometer were the moving belt interface and the direct liquid introduction (DLI) interface. The moving belt system relied on a moving mechanical transport device and the application of heat to introduce the solute while minimizing the introduction of a solvent. The initial versions were not very compatible with water as the mobile phase. Since reversed phase chromatography was especially in demand for polar type compounds, this incompatibility was a severe drawback. The DLI interface relied on splitting the HPLC eluent before introduction into the mass spectrometer, and consequently only a small percentage of the injected sample was ever detected.

The two most popular versions of HPLC in current usage are the thermospray interface and the particle beam interface. Thermospray (1) has been successfully applied for 5 or 6 years to a variety of compounds. Thermospray is an introduction technique, that with the aid of a volatile buffer, such as ammonium acetate, can also be an ionization technique. In short, the entire effluent of an HPLC at a flow of 1–1.5 mL/min enters the thermospray probe through a capillary tube which is electrically heated and in the process of heating and spraying, and with the use of a volatile buffer, charged droplets

are formed. When the electric field reaches a certain value and under the influence of the reduced pressure of the vacuum system, ion evaporation takes place which creates charged particles in the gas phase. Since the entire effluent of the HPLC has been introduced, an increased pressure of 2–10 Torr (3×10^{-3} to 1×10^{-2} atm) can be measured in the ion source. This situation is now amenable to ion-molecule reactions. Consequently, the ions that are detected are the result of these processes and little fragmentation is observed since little excess energy is deposited into the molecules. One or two ions characterize most spectra. The protonated molecule or ammonium adduct ion are usually the ions produced under thermospray ionization conditions. The protonated molecule dominates for compounds of high proton affinities (i.e., more basic in the gas phase than ammonia). For cationic compounds (M^+X^-), the M^+ ion is often observed.

The particle beam interface is a newer entry into HPLC/MS, but has already shown much potential for environmental analysis. The particle beam system which was derived from the monodisperse aerosol generation interface for combining liquid chromatography with mass spectrometry (MAGIC–LC/MS) (2) is capable of producing electron impact spectra. The particle beam systems rely on first generating an aerosol from the effluent of an HPLC. Various nebulizers have been used, including pneumatic and thermal. Next, most of the solvent is removed in the desolvation chamber which is an expansion region at high pressures (close to atmospheric pressure). Usually, a two-stage momentum separation that utilizes nozzles and skimmers and differential pumping enriches the solute in the aerosol beam. The solute will be vaporized by exposure to heated surfaces and ionized by electrons coming from a heated filament. The energy involved in this process is much greater than that which occurs in thermospray ionization and usually much fragmentation results. Therefore, electron impact spectra are produced which can be searched against libraries of electron impact spectra of standards.

Tandem mass spectrometry has been used (3) with thermospray to increase the structural information on compounds that is often missing with single stage MS. The use of collision activated dissociation (CAD) techniques in the tandem mass spectrometer produces fragmentation of the ion of interest. This process adds to the specificity of the HPLC/MS method under thermospray introduction.

In this report, the specific application of thermospray HPLC/MS and HPLC/MS/MS for the analysis of organic (azo) dyes and phenoxyacid herbicides in environmental samples will be discussed.

Organic dyes were chosen to test various modifications of the HPLC/MS systems that were used in these experiments. Dyes offer a wide range of structural functionalities and are often nonvolatile, even existing as salts in some uses, and therefore made good test compounds for HPLC/MS. Dyes are of environmental interest because of their wide use as colorants in a variety of products – from food to textiles. The dyes themselves or their synthetic intermediates, byproducts, and degradation products can be potential health hazards due to their toxicity or carcinogenicity or both. Dyes also make up approximately 10 percent of the new or newly-imported compounds in the United States undergoing Premanufacturing Notice (PMN) review.

Phenoxyaicd herbicides were chosen as a class of polar analytes that are not measured well by procedures currently listed in "Test Methods for Evaluating Solid Wastes (SW-846)." Methods 8150 and 8151 of the SW-846 manual both present protocols for determining certain chlorinated acid herbicides and their esters. These methods use gas chromatography (GC) with an electron capture detector to analyze sample extracts; Method 8150 specifies packed GC columns and Method 8151 prescribes the use of capillary GC columns. Both Methods 8150 and 8151 are labor-intensive and require the use of dangerous reagents, diazomethane or pentafluorobenzyl bromide, to convert the acids to their corresponding methyl esters prior to analysis. Because chlorophenoxy acids and their esters can be separated using HPLC directly (4), the hydrolysis and the derivatization steps are not required for LC/MS analysis.

SECTION 2

CONCLUSIONS

The use of HPLC methods to introduce compounds into a mass spectrometer offers the potential to monitor pollutants that were, heretofore, outside the scope of traditional analytical methods. Two important features that should characterize a mass spectral-based method for the analysis of environmental samples are sensitivity and specificity. Sensitivity may be compound dependent, but it can also change under different modes of ionization. This current work demonstrates the successful application of a wire-repeller to improve sensitivity in the positive ion thermospray mode, plus the alternative use of the negative ion (discharge on) mode with thermospray introduction for chlorinated or nitrated compounds with good sensitivity. Due to the addition of the wire-repeller in the ion source, the sensitivities for chlorinated phenoxy acid compounds in the positive thermospray ionization mode were comparable to those in the negative ion (discharge on) mode. The limits of detection (LOD) by positive thermospray ionization with a wire-repeller for a series of test dyes were improved by factors of 10–400 over the LOD's without this repeller. However, the negative ion (discharge on) mode, where applicable, was usually marked by increased fragmentation over the positive ion mode.

Other techniques were tried to increase the specificity of HPLC/MS. The specificity of a method depends upon the number of unique channels of information that the instrumentation provides. With mass spectral data specificity is determined by the fragmentation pattern produced for each compound. Daughter ion CAD MS/MS analyses on the thermospray ions have proved to be useful for determining structural identity. The drawback to using MS/MS techniques is the requirement to have a triple quadrupole MS or a multiple sector instrument. These instruments are expensive, but offer a variety of options which can help solve many analytical problems encountered in method development studies. For a more economical way of adding to the specificity of the method, a wire-repeller operated at 400 V was placed in the thermospray interface to induce fragmentation in the ion source. The spectra thus generated under this mode had similarities with both electron impact spectra and MS/MS CAD spectra. The sensitivity decreased compared with normal operation, however, when the system was operated in this manner.

Particle beam HPLC/MS offers the potential for generating useful structural data on a single quadrupole system by providing spectra similar to conventional electron impact mass spectra. Unfortunately, many compounds which are of interest for HPLC/MS, including dyes, do not have electron impact spectra recorded in commercial libraries.

The particle beam HPLC/MS system did not have the sensitivity exhibited by the thermospray HPLC/MS system. In this present work, the differences were sometimes three to four orders of magnitude greater for the thermospray system for a series of dyes. There were various reasons for these differences, but improvements in the optimization of the particle beam system and interface design should make the variance in sensitivities smaller.

The general conclusion of this work is, at the present time, thermospray HPLC/MS and particle beam HPLC/MS remain complementary techniques, each offering something unique in its application. For work that involves trace analysis, thermospray HPLC/MS would be the choice. For structural identification or confirmation on a single quadrupole mass spectrometer, one would use the particle beam HPLC/MS system (or thermospray with a wire-repeller). Lastly, the triple quadrupole mass spectrometer remains a versatile system for structural identity, especially when used in conjunction with thermospray HPLC/MS.

SECTION 3

RECOMMENDATIONS

The particle beam HPLC/MS system needs further study. The method sensitivity obtained in the present study for dyes has been disappointing using instrumentation available at the Laboratory. Newer equipment, including dedicated particle beam HPLC/MS systems were evaluated for their sensitivity for compounds of environmental interest. When spectra of compounds are in a computerized standard library, the electron impact (EI) spectra that are generated by the particle beam system appear to match those in the library. Too many compounds that are of interest with HPLC methods, however, are not in the standard library. Work on adding to this data base needs to be accomplished.

The development of repeller-induced (CAD) spectra generated on thermospray is promising, but again needs further work to improve the limits of detection in this mode.

HPLC/MS methods with spatial tandem mass spectrometers may be too expensive for the average laboratory. The development of the temporal tandem mass spectrometers, especially the ion trap, holds potential for interfacing both particle beam and thermospray systems at a significant cost reduction. This would allow the analyst to perform MS^n on an ion of choice to gather structural information.

SECTION 4

EXPERIMENTAL PROCEDURES

GENERAL PROCEDURES

Thermospray Ionization HPLC/MS and HPLC/MS/MS

The instrument used in these experiments was a Finnigan MAT TSQ®45 triple quadrupole mass spectrometer equipped with a modified Vestec ion source and thermospray interface. The modification in the Vestec ion source consisted of the addition of a wire-repeller (5,6). A hole was drilled exactly opposite the ion-extraction funnel and a 0.64-mm diameter copper wire, insulated with a ceramic tube, was introduced. This wire-repeller was operated in two configurations. The first configuration, which is shown on Figure 1, was devised to maximize the sensitivity of thermospray ionization. The wire faces the funnel but does not protrude into the ion chamber volume. When a voltage is applied to the repeller with respect to the funnel (ground potential), a directed, narrow electric field produced between the wire and the funnel. The sensitivity of the instrument maximized between 200 and 250 V.

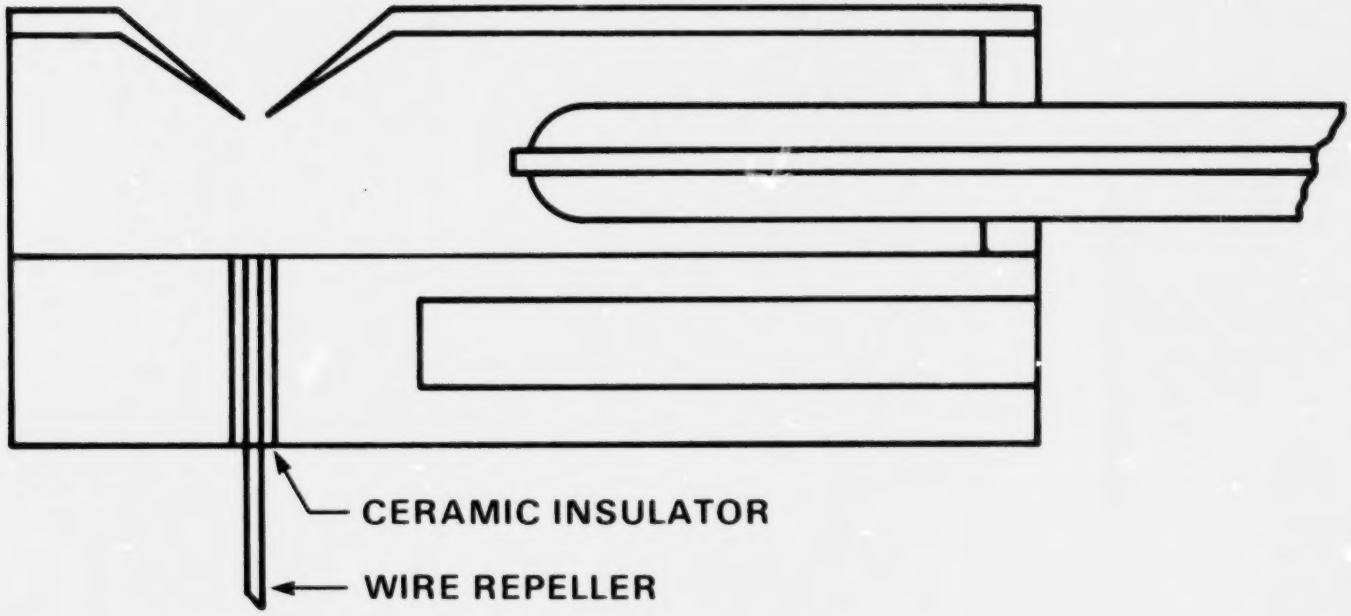
When the wire-repeller was operated in the other configuration (Figure 2), increased fragmentation resulted. The wire-repeller in this case was inserted approximately 4 mm into the ion chamber and was operated at 400 V.

The HPLC instrumentation consisted of a Rheodyne Model 7125 injector valve fitted with a 10-µL sample loop and a Spectra-Physics SP8700XR solvent delivery system. A flow of 0.4 mL/min was used through a 15 cm x 2 mm ODS Hypersil 5-µm analytical column from Keystone Scientific or a 15 cm x 2.1 mm LC-18 5-µm analytical column from Supelco. A syringe pump (ISCO LC-5000) was connected to the system to deliver the buffer - 0.1 M ammonium acetate – post column at a flow of 0.88 mL/min via the thermospray interface into the ion source. With this arrangement two injection options were allowed: direct flow injection bypassing the column and chromatographic separation onto the column. For direct flow injections the mobile phase was methanol-water (50:50). On column injections were made with a solvent program of 100% water to 100% methanol in 10 minutes with a 15-minute hold. Typical operating conditions of the thermospray interface were as follows:

T (vaporizer) = 120–130°C; T (tip) = 190–235°C;
T (source) = 230–250°C; T (jet) = 200–220°C.

Polyethylene glycol (Aldrich), average molecular weight 400, was used to calibrate the mass spectrometer. The scan time was 1.5 sec.

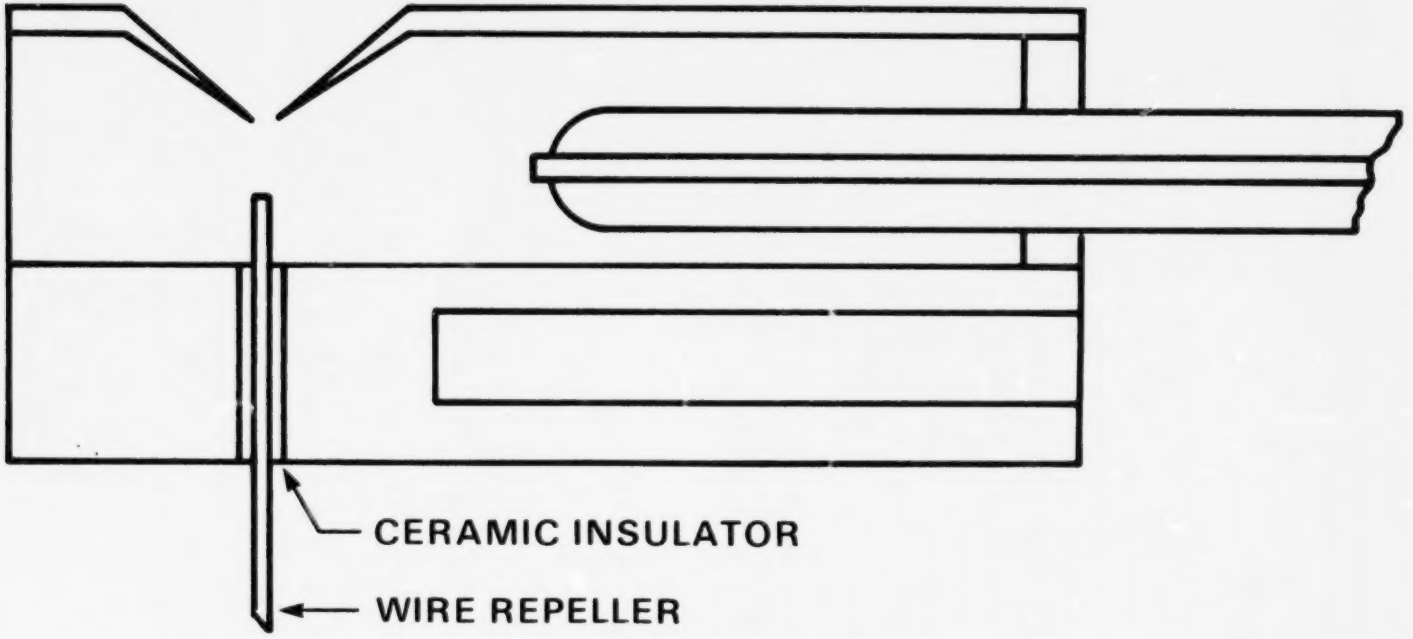
Thermospray Source With Wire Repeller



a. Sensitivity Enhancement Configuration 200-250 V

Figure 1. Schematic diagram of thermospray ion source with wire-repeller (sensitivity enhancement configuration).

Thermospray Source With Wire Repeller



b. Repeller-CAD Configuration

Figure 2. Schematic diagram of thermospray ion source with wire-repeller (repeller-induced dissociation configuration).

The CAD experiments in the tandem mass spectrometry (MS/MS) mode were conducted at a collision energy of 20 eV and a pressure of argon of approximately 1 mTorr.

Particle Beam HPLC/MS

A Finnigan MAT TSQ®45 triple quadrupole mass spectrometer equipped with a 4510 electron impact/chemical ionization (EI/CI) ion source was used. The particle beam HPLC/MS interface was an Extrel ThermaBeam™. The interface was fitted to the ion source of the mass spectrometer by means of a machined adapter which is shown in Figure 3. This heatable adapter, made partly of brass and mainly of Vespel (Dupont) and approximately 8 cm in length, was heated to 200–250°C. The ion source was operated at 240°C. The filament emission current was 0.3 mA and the electron multiplier voltage was 1600 V. The preamplifier sensitivity was set at 10^{-8} A/V. The ThermaBeam™ nebulizer temperature was 210–240°C. This temperature varied with composition of the mobile phase gradient. The ThermaBeam™ expansion chamber temperature was 95°C. The HPLC consisted of a Spectra-Physics SP8700XR solvent delivery system with a Rheodyne Model 7125 injector valve fitted with a 10-µl sample loop. The column was a 15 cm x 4 mm Varian Micro Pak MCH-5-N-CAP C18 column. The HPLC was operated in the gradient mode, starting at a mobile phase of methanol-water (50:50), changing within 5 minutes to 100 percent methanol, and holding at that level for 10 minutes. The flow rate was 0.9 mL/min.

MATERIALS

The following dyestuffs (Figure 4), identified by their Colour Index (C.I.) name, were obtained from the sources indicated and were used without further purification: 1-6, 8, 9, 12-15, and 20 (Aldrich Chemical Company, Milwaukee, Wisconsin); 7, 10, and 19 (Sandoz Colors and Chemicals, Charlotte, North Carolina); 18 (Ciba-Geigy Dyestuffs and Chemicals Division, Greensboro, North Carolina); 16 (Pylam Products Co., Garden City, New York); 11 (Chem Services, Inc., West Chester, Pennsylvania).

The dyes were dissolved in an appropriate solvent prior to analysis; dyes 1, 3-5, 7, 9, 12, 14-16, and 20 in acetonitrile-water (50/50, v/v), dyes 2, 8, 10, 11, and 17 in methanol, dyes 6 and 18 in acetonitrile, dye 13 in methylene chloride-acetonitrile (30/70, v/v) and sample 19 in methylene chloride-acetonitrile (50:50, v/v).

Solutions of standards in methanol were prepared from herbicides (Figure 5) received from the Pesticide and Industrial Chemicals Repository, U.S. Environmental Protection Agency Repository (Research Triangle Park, North Carolina).

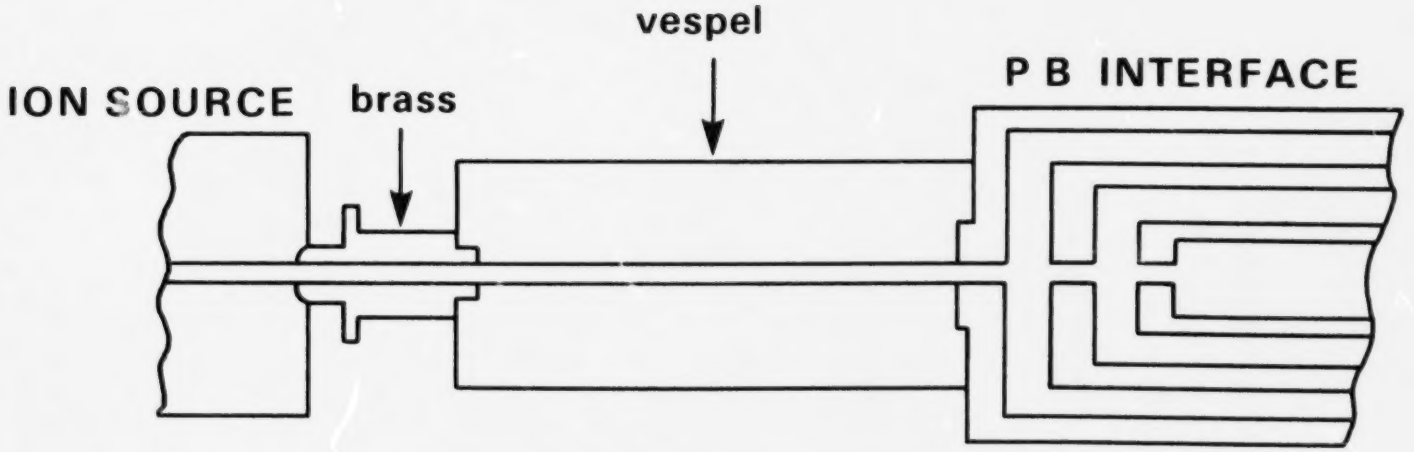
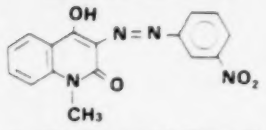
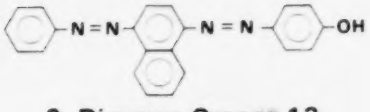


Figure 3. Particle beam HPLC/MS adapter. Heater wires are placed in drilled holes along the axis in the Vespel (not shown in figure).

AZO CLASS



1. Disperse Yellow 5
C.I. 12790



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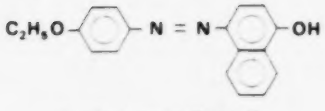
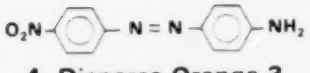
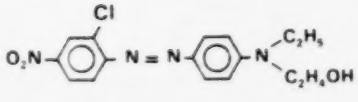
C.I. 26080



3. Solvent Red 3
C.I. 12010



4. Disperse Orange 3
C.I. 11005



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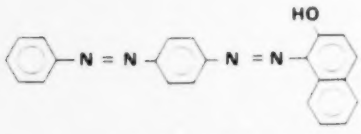
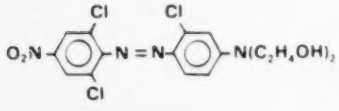
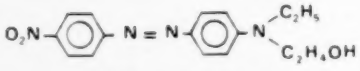
C.I. 11115



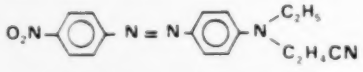
6. Solvent Red 23
C.I. 26100



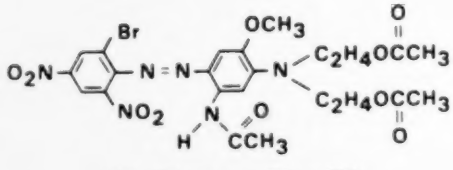
7. Disperse Brown 1
C.I. 11152



8. Disperse Red 1
C.I. 11110



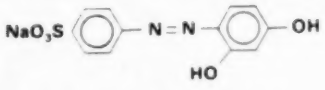
9. Disperse Orange 25
C.I. 11227



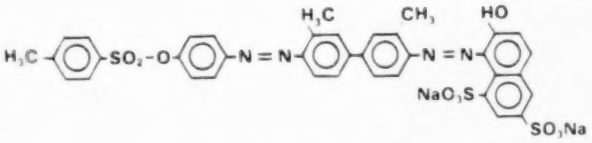
10. Disperse Blue 79
C.I. None

Figure 4. Structures of dyes.

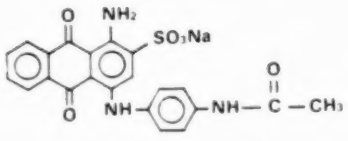
SULFONATED AZO CLASS



11. Acid Orange 6
C.I. 14270

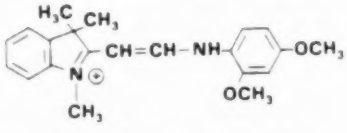


15. Acid Red 114
C.I. 23635

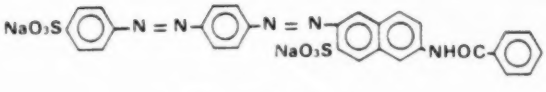


12. Acid Blue 40
C.I. 62125

METHINE CLASS

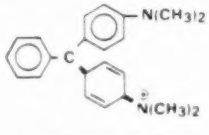


16. Basic Yellow 11
C.I. 48055

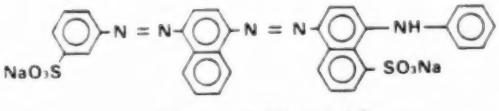


13. Direct Red 81
C.I. 28160

ARYLMETHANE CLASS



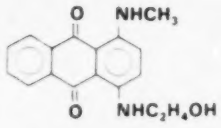
17. Basic Green 4
C.I. 42000



14. Acid Blue 113
C.I. 26360

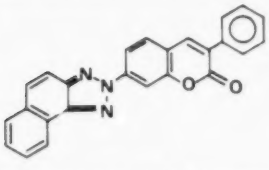
Figure 4. Structures of dyes. (Continued)

ANTHRAQUINONE CLASS



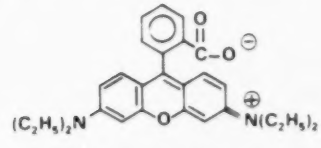
18 Disperse Blue 3
C.I. 61505

COUMARIN CLASS



19 Fluorescent Brightener 236
C.I. None

XANTHENE CLASS



20 Solvent Red 49
C.I. 45170.1

Figure 4. Structures of dyes. (Continued)

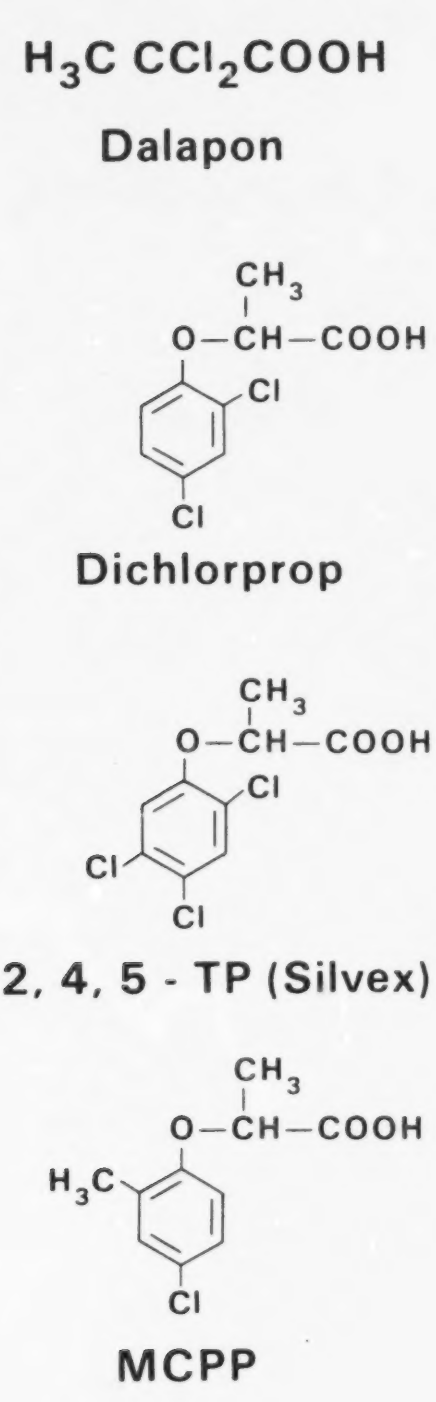
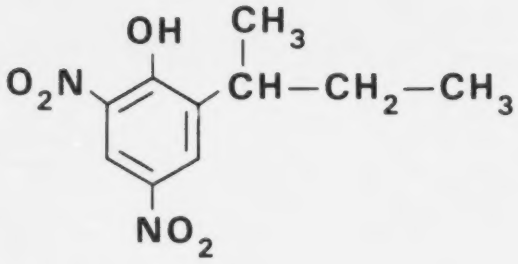
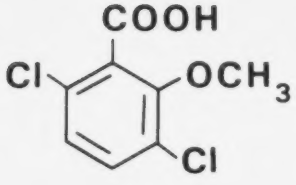


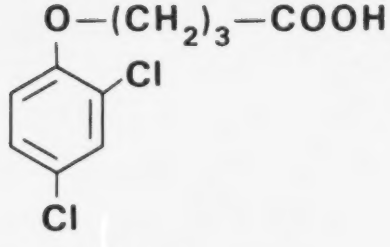
Figure 5. Structures of herbicides.



Dinoseb

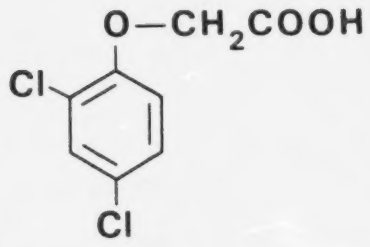


Dicamba

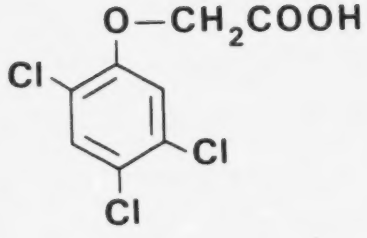


2, 4 - DB

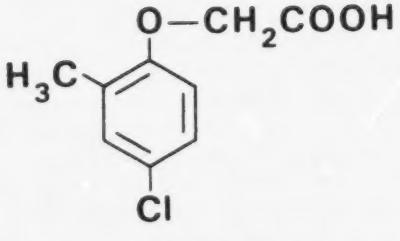
Figure 5. Structures of herbicides. (Continued)



2, 4 - D



2, 4, 5 -T



MCPA

Figure 5. Structures of herbicides. (Continued)

SECTION 5

RESULTS AND DISCUSSION

DYES

The detection limits of commercial dyes are reported in Table 1. Commercial dyes are formulations and are often not pure. The approximate purity of each dye is listed in this table. The dyes were not further purified, and the limits of detection were not corrected for purity and, therefore, should be regarded as an upper limit. The limits of detection were obtained by recording the ion current traces at characteristic masses of the dyes under full-mass scan with a signal-to-noise ratio of at least three. An example is given in Figure 6, which shows the ion current traces of the two major ions of Disperse Blue 3, $[M+H]^+$ at $^m/_z$ 297 and $[M+H-NHCH_3]^+$ at $^m/_z$ 267. These ion traces were obtained by multiple direct injections of 50 pg samples at repeller 220 V. All the dyes were sampled through direct flow injection analysis, bypassing the analytical column, under thermospray ionization conditions. Each dye was injected separately through the HPLC under particle beam conditions.

Also included in this table are limits of detection for six of the dyes that were previously obtained under thermospray ionization with an ion source without a repeller (3). Enhancement factors of between 10 and 400 were observed for the configuration with the wire-repeller. The comparison of thermospray ionization with repeller and the particle beam system shows differences in limits of detection between the two methods of between 20 and 16,000 in favor of thermospray ionization. There are several reasons for this difference. These numbers may reflect that the system was optimized for thermospray ionization while the connection between the ThermaBeam™ particle beam interface and the Finnigan mass spectrometer was fabricated in our laboratory. This must be considered a hybrid system. For reference, the limit of detection for caffeine with this hybrid system was 15 ng. Preliminary results on a dedicated particle beam HPLC/MS system indicate better limits of detection by 2 to 10 times for these dyes over that presented here. Another reason for these differences in limits of detection is the consideration that the quantification ion used under thermospray ionization was the $(M+H)^+$ ion for each of these dyes. This ion was very intense and often was the only ion in the mass spectrum of a particular dye. Under particle beam HPLC/MS, no such intense ion exists and the total ionization has been spread among many ions. A third reason is the intrinsic differences between the thermospray ionization and particle beam systems. In the thermospray system, with buffer assisted ionization, all the effluent from the HPLC is directed into the ion source. At the pressures that occur under this situation (2-10 Torr), ion-molecule reactions take place. Since these types of reactions are very efficient - one reaction per collision - the product

TABLE 1. DETECTION LIMITS FOR COMMERCIAL DYES

Dye	Structure	MW	Dye Content (%)	TSP (w/o repeller) Detection Limit* (ng)	TSP (with repeller) Detection Limit* (ng)	PB LC/MS Detection Limit** (ng)
Disperse Yellow 5	1	324	C.30	-	5	500
Disperse Orange 13	2	352	C.15	150-200	20	5500
Solvent Red 3	3	292	100	-	10	200
Disperse Orange 3	4	242	C.20	-	2.5	50
Disperse Red 13	5	348	C.25	-	10	4400
Solvent Red 23	6	352	C.85	50	5	500
Disperse Brown 1	7	432	C.25	-	10	2700
Disperse Red. 1	8	314	C.30	-	0.1	250
Disperse Orange 25	9	323	C.20	-	10	500
Disperse Blue 79	10	624	100	250-500	10	300
Basic Green 4	17	329	C.98	20	0.67	700
Disperse Blue 3	18	296	C.20	20	0.05	800
Fluorescent Brightener 236	19	389	100	25-50	4	600
Solvent Red 49	20	442	C.97	-	1	500

*Flow injection analysis
**On column injection

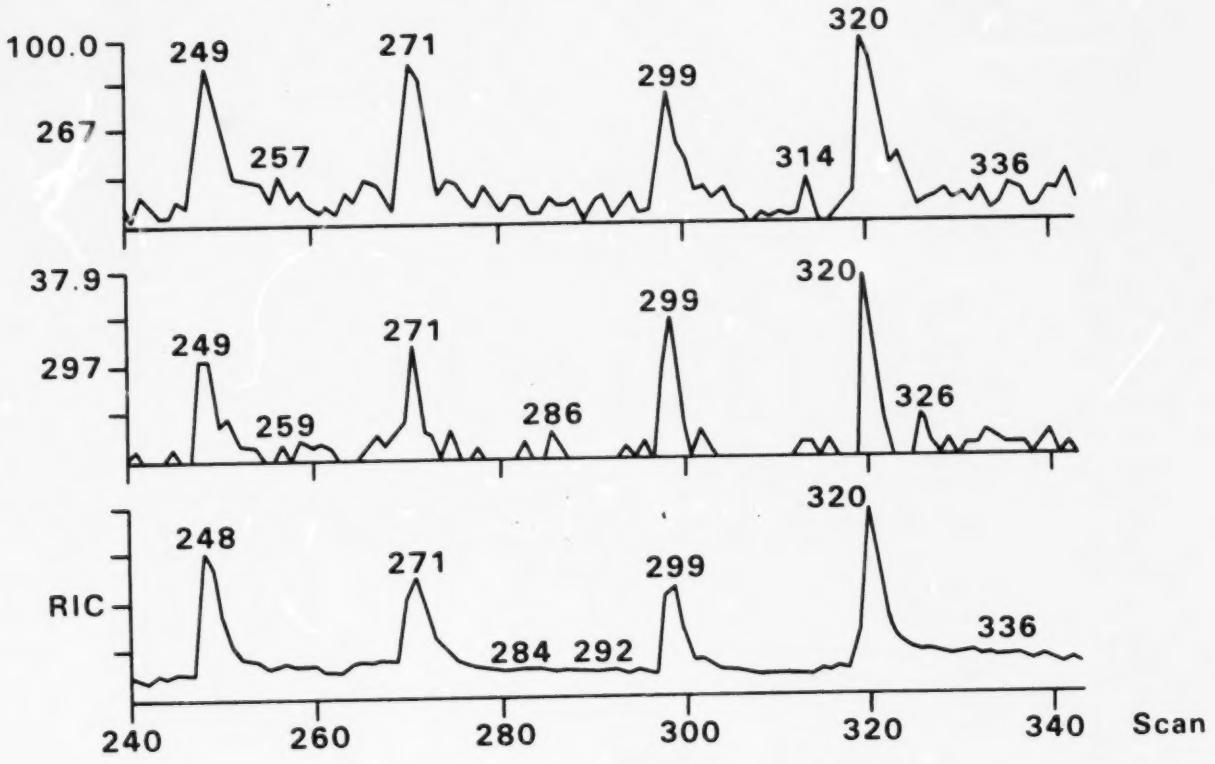


Figure 6. Reconstructed ion current traces of ions at $^{m}/_{z}$ 297 and $^{m}/_{z}$ 267, and the total reconstructed ion current, following four successive injections of 50 pg of Disperse Blue 3.

ion, $(M+H)^+$, becomes very intense. Since the particle beam system was designed to remove most of the solvent before the solute enters the ion source, natural losses of analyte being pumped away with the solvent could occur. Lastly, the LOD's were measured under flow injection conditions for the thermospray system and on column for the particle beam interface.

Because of the increased sensitivity of the system with the use of the wire-repeller, the thermospray positive ion mass spectra of several sulfonated azo dyes could be recorded for the first time. Azo dyes are sulfonated to make them water soluble, so direct dyes and acid dyes are usually sulfonated. These sulfonated dyes exist as salts (often sodium salts) and the characteristic part of the dye is anionic in solution. Consequently, the negative ion mass spectra of some sulfonated azo dyes have been reported (7,8). Sulfonated azo dyes have been difficult to analyze by thermospray techniques, however, recent advances in ion spray and electrospray interfaces with atmospheric pressure ionization have made it easier to characterize these dyes under the negative ion mode (9). The results of the positive ion thermospray ionization for four sulfonated azo dyes are summarized in Table 2. The characteristic ions are those formed from losses of SO_3Na and $2SO_3Na$ as well as losses of Na and 2Na. The loss of each one of these groups involves the replacement by a hydrogen atom. Acid Blue 40, which has only one SO_3Na group, and Acid Red 114, which has two SO_3Na groups attached to the same ring, lose one and two SO_3Na groups, respectively. Direct Red 81 and Acid Blue 113, each having two SO_3Na groups on different rings, lose both one and two Na atoms, but do not appear to lose SO_3 groups, which seem to be more strongly attached to the molecules.

The particle beam EI mass spectra of six azo dyes are compiled in Table 3. As can be seen in this table, more ions are generated by the particle beam system than by buffer-assisted thermospray ionization in which each spectrum is usually characterized by one or two ions. However, the use of CAD in tandem MS can generate similar numbers of fragment ions. Table 4 lists the daughter ions produced by CAD of $(M+H)^+$ ions of these same dyes in the thermospray system. Disperse Blue 79 is an unusual compound as both the EI and CAD mass spectra show only one ion at $^m/_z$ 87, which is $CH_3COOC_2H_4^+$. Each of these six azo dyes give approximately the same degree of fragmentation under EI and CAD conditions. Most of the compounds show enough fragmentation under either mode that these dyes can be identified by library searches or structural interpretation. These compounds generally show diagnostic ions which are characteristic of azo dyes. These ions are associated with cleavage at the azo linkage at the C-N or N-C bond or at the N-N bond, e.g., $^m/_z$ 92 (aminophenyl ion) and 122 (nitrophenyl ion) for Disperse Orange 3 under the CAD mode and $^m/_z$ 92 (aminophenyl ion) under the particle beam EI mode.

An interesting EI mass spectrum generated from the particle beam system is that of Basic Green 4 (Malachite Green) which is shown in Figure 7. This spectrum includes an ion at $^m/_z$ 329 which is the molecular cation. The ion at $^m/_z$ 330 is the ion representing the leuco compound, that is, the reduced neutral form of the cationic dye generated by the addition of a hydride ion to the cation. The ion at $^m/_z$ 126 was believed to be the doubly-charged ion $[M-C_6H_5]^{2+}$. Since the particle beam interface was attached to a triple quadrupole MS, CAD experiments could be performed on this ion. The resulting

TABLE 2. THERMOSPRAY IONIZATION POSITIVE ION SPECTRA OF SULFONATED AZO DYES

Compound	MW	% Relative Abundance				
		$[MH]^+$	$[MH-Na+H]^+$	$[MH-2Na+2H]^+$	$[MH-NaSO_3+H]^+$	$[MH-2NaSO_3+2H]^+$
Acid Blue 40	473	1.3	0.4	--	100	--
Direct Red 81	675	20	88	100	--	--
Acid Blue 113	681	15	33	100	--	*
Acid Red 114	830	--	--	--	--	100

*Not measured

TABLE 3. PARTICLE BEAM EI MASS SPECTRA OF AZO DYES

Dye	MW	$^{m}/_{z}$ of ions observed (% relative abundance)
Disperse Blue 79	624	87(100)
Disperse Yellow 5	324	324(1), 295(1.5), 202(3), 174(7), 138(9), 108(100), 92(17)
Solvent Red 3	292	292(17), 263(3), 235(4), 171(6), 149(9), 143(100), 121(48), 115(36), 108(18)
Disperse Orange 3	242	242(3), 213(4), 212(10), 120(55), 92(100)
Disperse Red 13	348	317(22), 287(20), 154(17), 144(25), 142(28), 134(25), 133(100), 126(40), 120(30), 105(50), 104(50), 99(20), 92(32), 90(40)
Disperse Brown 1	432	432(1.5), 403(15), 402(5), 401(17), 359(5.5), 357(7), 313(5), 214(15), 208(17), 206(36), 185(40), 183(78), 176(39), 167(32), 149(77), 139(100), 124(49), 104(82), 90(48)

CAD spectrum of $^{m}/_{z}$ 126 is shown on Figure 8. The most intense daughter ion is at $^{m}/_{z}$ 118. This loss of 8 apparent mass units can be explained only by both ions being double charged, and, therefore, the ion at $^{m}/_{z}$ 118 is due to the loss of CH_4 (16 mass units) thus forming the $[M-C_6H_5-CH_4]^{2+}$ ion. Both of these doubly-charged ions are double imminium ions. No ions above $^{m}/_{z}$ 126 were observed in this CAD experiment.

Several studies (10-12) were made on the use of a repeller in order to increase the fragmentation of the mass spectra in thermospray ionization. The increased fragmentation in the spectra were interpreted as resulting from CAD of the $(M+H)^+$ ion.

The same wire-repeller that was used to enhance sensitivity in the buffer-enhanced thermospray ionization mode was used to obtain repeller-CAD spectra. In order for proper operation, the wire-repeller had to be pushed into the ion source by approximately 4 mm and the power supply set for 400 V. Table 5 summarizes the fragmentation produced for three azo dyes. These spectra were obtained with 3.6-10 µg of material injected directly into the system. A comparison of this table with Tables 3 and 4 shows similarities between these spectra and the EI and MS/MS CAD spectra. Again, similar trends in degree of fragmentation are apparent as Disperse Orange 3 does not show such fragmentation and Disperse Brown 1 shows abundant fragmentation. Typical MS/MS CAD ions such as $^{m}/_{z}$ 357, 218, 197, 183, 166, 153, 140, and 139 are present. Fragment ions similar to those observed in EI are at $^{m}/_{z}$ 401, 357, 183, and 139. Masses below $^{m}/_{z}$ 120 were not recorded due to increased solvent background in this region of the spectrum.

TABLE 4. CAD SPECTRA OF $(M+H)^+$ IONS OF AZO DYES GENERATED BY THERMOSPRAY IONIZATION

Dye	$[M+H]^+$	m/z of ions observed (% relative abundance)
Disperse Blue 79	625	87(100)
Disperse Yellow 5	325	325(34), 279(5.7), 187(100), 138(23), 116(13), 67(8.5)
Solvent Red 3	293	293(6.2), 143(42), 139(5.1), 121(100), 115(8.2), 111(6.3), 108(6.6), 103(5.7), 93(5.7), 91(34), 77(44), 65(19)
Disperse Orange 3	243	243(13), 197(11), 140(5.1), 122(100), 93(8.2), 92(32), 76(8.9), 75(27)
Disperse Red 13	349	349(97), 318(14), 303(14), 289(24), 178(37), 156(12), 147(44), 134(10), 120(8.2), 119(6.8), 106(5.4)
Disperse Brown 1	433	433(63), 402(17), 387(8.3), 357(23), 311(9.4), 228(20), 218(12), 197(100), 193(12), 190(37), 185(55), 184(6.9), 183(10), 180(5.5), 166(15), 163(33), 161(8.3), 158(30), 153(92), 152(6.9), 147(6.2), 145(8.3), 144(14), 143(5.5), 140(6.9), 139(7.9), 131(5.5), 128(5.5), 126(7.9), 122(5.5), 120(12), 119(15), 118(17), 117(5.5), 116(6.2), 114(59), 113(6.2), 107(13), 99(18), 70(25) 45(8.3)

CHLORINATED HERBICIDES

The positive ion thermospray mass spectra of the chlorinated herbicides plus dinoseb are summarized in Table 6. The base peak in all cases is the $(M+NH_4)^+$ ion; for two compounds, 2,4-DB and dinoseb, the $(M+H)^+$ ion is present. No ions were detected for dalapon. Since the protonated molecule is present for both 2,4-DB and dinoseb, these compounds have the highest apparent proton affinities among these herbicides.

Voyksner reported 10-µg positive ion thermospray detection limits for similar compounds (13). Due to the increased sensitivity produced by the wire-repeller in the present work, quantities between 2.7 and 170 ng of the compounds in Table 6 could be observed in the positive ion thermospray mode (Table 7).

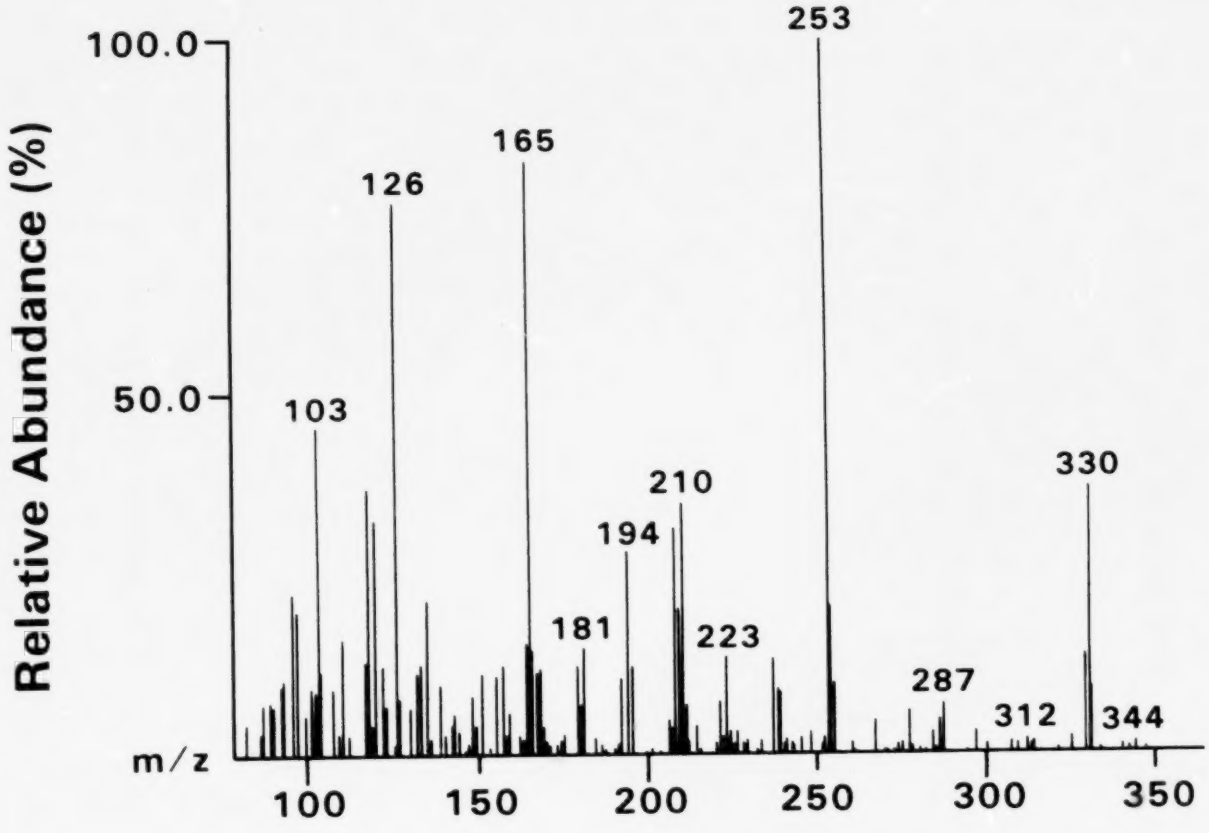


Figure 7. EI mass spectrum of Basic Green 4.

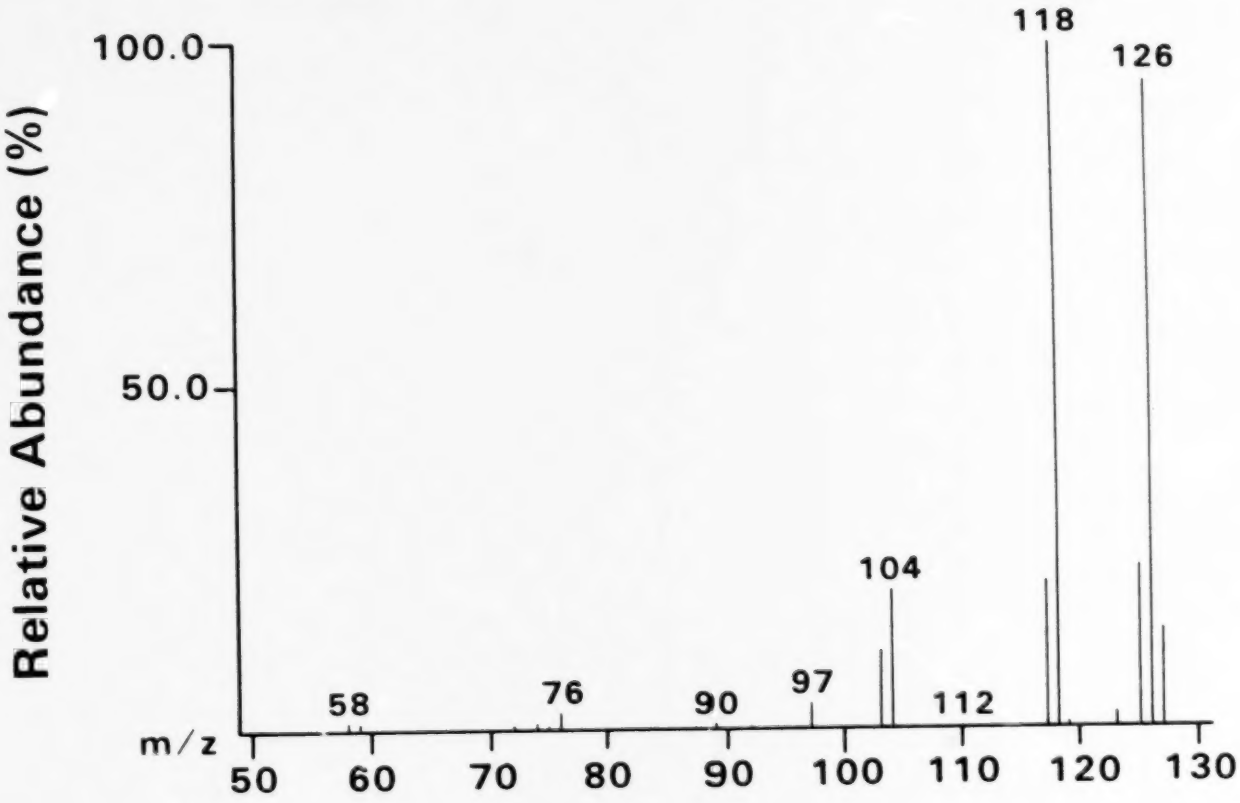


Figure 8. CAD spectrum of the ion at $^{m}/_{z}$ 126 in Basic Green 4.

TABLE 5. THERMOSPRAY IONIZATION REPELLER-INDUCED CAD MASS SPECTRA OF AZO DYES

Dye	$[M+H]^+$	m/z of ions observed (% relative abundance)
Solvent Red 3	293	293(59), 292(31), 263(6), 207(7), 161(7), 160(23), 159(16), 158(18), 157(11), 144(9), 143(100), 139(14), 138(32)
Disperse Orange 3	243	243(100), 226(10), 197(8)
Disperse Brown 1	433	433(53), 417(11), 401(64), 385(32), 371(13), 357(100), 355(48), 313(21), 231(21), 218(16), 207(27), 197(32), 183(74), 172(16), 170(14), 166(21), 153(56), 140(36), 139(90), 134(45), 131(14), 130(14), 124(19)

TABLE 6. POSITIVE ION THERMOSPRAY MASS SPECTRA OF CHLORINATED ACID HERBICIDES

Compound	RT	MW	Mass Spectra (% Rel. Abund.)
Dicamba	2:42	220	$(M+NH_4)^+$ (100)
2,4-D	9:16	220	$(M+NH_4)^+$ (100)
MCPA	9:30	200	$(M+NH_4)^+$ (100)
Dichlorprop	10:40	234	$(M+NH_4)^+$ (100)
MCPP	10:45	214	$(M+NH_4)^+$ (100)
2,4,5-T	11:09	254	$(M+NH_4)^+$ (100)
2,4,5-TP	11:46	268	$(M+NH_4)^+$ (100)
2,4-DB	12:43	248	$(M+NH_4)^+$ (100), $(M+H)^+$ (35)
Dinoseb	16:09	240	$(M+NH_4)^+$ (100), $(M+H)^+$ (70)

TABLE 7. LIMITS OF DETECTION IN THE POSITIVE AND NEGATIVE ION MODES FOR THE CHLORINATED ACID HERBICIDES

Compound	Positive Mode Quantification Ion	LOD (ng)	Negative Mode Quantification Ion	LOD (ng)
Dalapon	Not detected	-	$141(M-1)^-$	11
Dicamba	$238(M+NH_4)^+$	13	$184(M-HCl)^-$	3.0
2,4-D	$238(M+NH_4)^+$	2.9	$219(M-1)^-$	50
MCPA	$218(M+NH_4)^+$	120	$199(M-1)^-$	28
Dichlorprop	$252(M+NH_4)^+$	2.7	$235(M-1)^-$	25
MCPP	$232(M+NH_4)^+$	5.0	$213(M-1)^-$	12
2,4,5-T	$272(M+NH_4)^+$	170	$218(M-HCl)^-$	6.5
2,4,5-TP	$286(M+NH_4)^+$	160	$269(M+1)^-$	43
Dinoseb	$228(M+NH_4-NO)^+$	24	$240(M)^-$	19
2,4-DB	$266(M+NH_4)^+$	3.4	$247(M-1)^-$	110

Since two ions per compound at most are generated in the positive ion mode, little structural information is obtained from these spectra. Consequently, three options to the single quadrupole positive ion thermospray mode were tested: (1) the negative ion "discharge on" mode; (2) daughter ion CAD in the MS/MS mode of the $(M+NH_4)^+$ ions, and (3) repeller-induced CAD in the positive ion single quadrupole mode.

Since these compounds were chlorinated or nitrated and consequently had high electron affinities, they were considered good candidates for negative ion detection. The results of "discharge on" negative ion mode are summarized in Table 8. The possible assignments of ions are listed for those fragments greater than 15 percent relative abundance. Along with a fairly intense $(M-H)^-$ ion, significant fragmentation occurs in these examples. Losses of Cl and (CH_2) COOH from the $(M-H)^-$ ion form the majority of the fragment ions. The limits of detection ranged from 3 to 110 ng and are summarized in Table 7.

The information generated in the MS/MS mode of operation of the triple quadrupole mass spectrometer for these chlorinated herbicides is typified by the spectrum shown in Figure 9. This figure represents the daughter ion CAD spectrum of the $^{m}/_{z}$ 266 ion from 2,4-DB. The $(M+NH_4)^+$ ion at $^{m}/_{z}$ 266 was generated in the positive ion thermospray ionization mode of 2,4-DB. Losses of OH (or NH_3), Cl (or NH_3 and H_2O), and (CH_2) $COOH \cdot NH_4$ from the ammoniated species comprise the majority of the ions in the spectrum; $(CH_2)_3COOH^+$ is the base peak. Since the $^{m}/_{z}$ 266 ion has only contributions from ^{35}Cl, the CAD spectrum is not marked by the chlorine isotopic pattern that these herbicides usually show. Consequently, a simpler spectrum results.

Figures 10 and 11 show the single quadrupole CAD spectra of 2,4-D and 2,4-DB, respectively, which were generated using the wire-repeller at 400 V. This spectrum for 2,4-D shows similarities with its electron impact spectrum (14), as $^{m}/_{z}$ 162 $(C_6H_3Cl_2OH)^+$ is the base peak in both cases. Also, comparing the MS/MS CAD spectrum of 2,4-DB (Figure 9) with the repeller-induced CAD spectrum (Figure 11) is instructive. It appears that the $^{m}/_{z}$ 231 ion, which is a major peak in both spectra, is due to the loss of H_2O from the $(M+H)^+$ ion, rather than the loss of Cl from the $(M+NH_4)^+$ ion. The repeller-induced CAD spectrum shows the same isotopic pattern for both the $(M+1)^+$ ion and the $(M+1-18)^+$ ion. The $^{m}/_{z}$ 162 peak is very intense in the repeller-induced CAD spectrum while this peak does not appear in the MS/MS CAD spectrum. The $(CH_2)_3COOH^+$ ion is the base peak in both spectra.

Table 9 presents the repeller-induced CAD mass spectra for nine acid herbicides. Again, possible ions are assigned for those peaks greater than 15 percent relative abundance.

Finally, Table 10 compares the Method Detection Limits of the herbicides in Method 8150 with those achieved by using direct analysis by HPLC/MS. For seven of these ten compounds the HPLC/MS give equal or better MDL's than the GC based method.

TABLE 8. NEGATIVE ION MASS SPECTRA OF CHLORINATED ACID HERBICIDES (DISCHARGE ON)

Compound	MW	Mass Spectra (% Relative Abundance)
Dalapon	142	$(M-H)^-$(100), $(M+OAc)^-$(25)
Dicamba	220	$(M-H)^-$(33), M^-(39), $(M+H)^-$(33), $(M-HCl)^-$(100), $(M-Cl)^-$(60), $(M-CH_2Cl)^-$(31), $(M-H_2Cl_2)^-$(45)
2,4-D	220	$(M-H)^-$(100), M^-(60), $(M-HCl)^-$(60), $(M-Cl)^-$(35), $(M-HCOOH)^-$(43)
MCPA	200	$(M-H)^-$(100), $(M+HCO_2)^-$(10),
Dichlorprop	234	$(M-H)^-$(100), M^-(17), $(M-HCl)^-$(30), $(M-Cl)^-$(20), $(M-CH(CH_3)COOH)^-$(22),
MCPP	214	$(M-H)^-$(100), $(M+HCO_2)^-$(7)
2,4,5-T	254	$(M-H)^-$(27), M^-(27), $(M+H)^-$(31), $(M-HCl)^-$(100), $(M-Cl)^-$(22), $(M-HCOOH)^-$(18), $(M-CH_2COOH)$(15), $(M+H-CH_2COO)^-$(33), $(M-Cl-COOH)^-$(38), $(M-Cl-CHCOOH)^-$(23)
2,4,5-TP	268	$(M-H)^-$(36), M^-(13), $(M+H)^-$(73), $(M-HCl)^-$(83), $(M-Cl)^-$(28), $(M-HCl_2)$(100), $(M-CH(CH_3)COOH)^-$(28), $(M+H-Cl_2)^-$(58), $(M-Cl-C(CH_3)COOH)^-$(35), $(M-H_2Cl_3)^-$(31)
2,4-DB	248	$(M-H)^-$(100), M^-(10), $(M+HCO_2)^-$(20) $(M-(CH_2)_3CO_2H)^-$(77)
Dinoseb	240	$(M-H)^-$(45), M^-(100), $(M-OH)^-$(42)

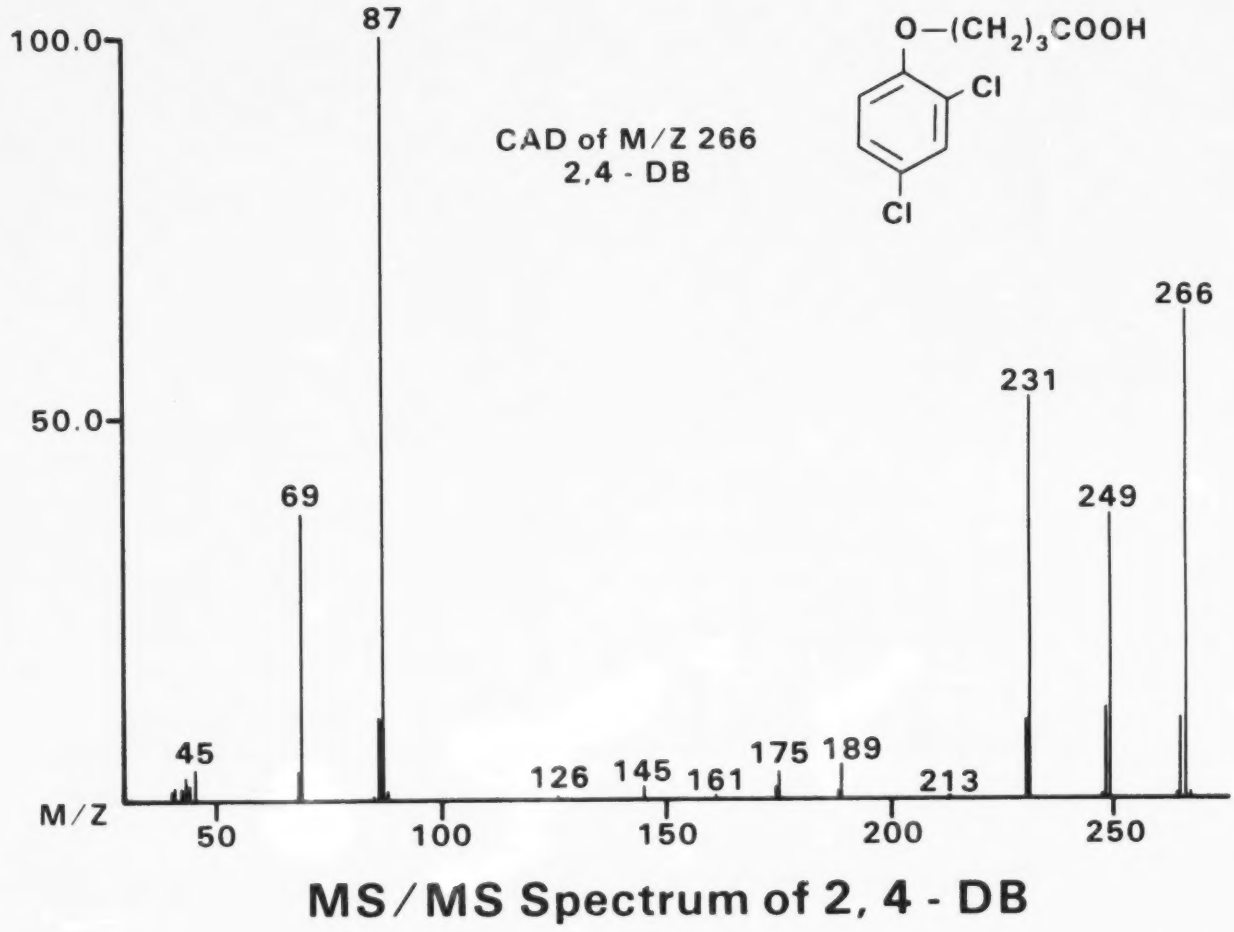


Figure 9. MS/MS Spectrum of 2,4-DB.

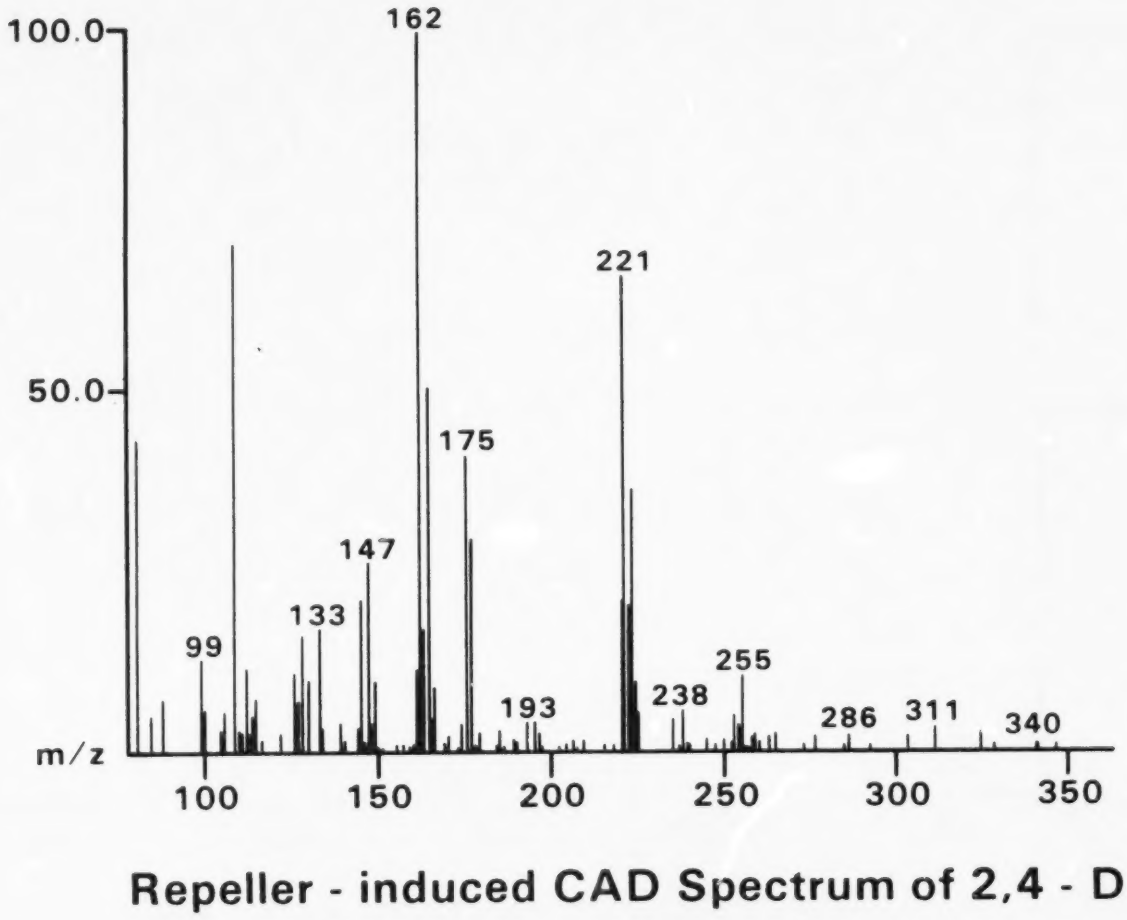


Figure 10. Repeller-induced CAD spectrum of 2,4-D.

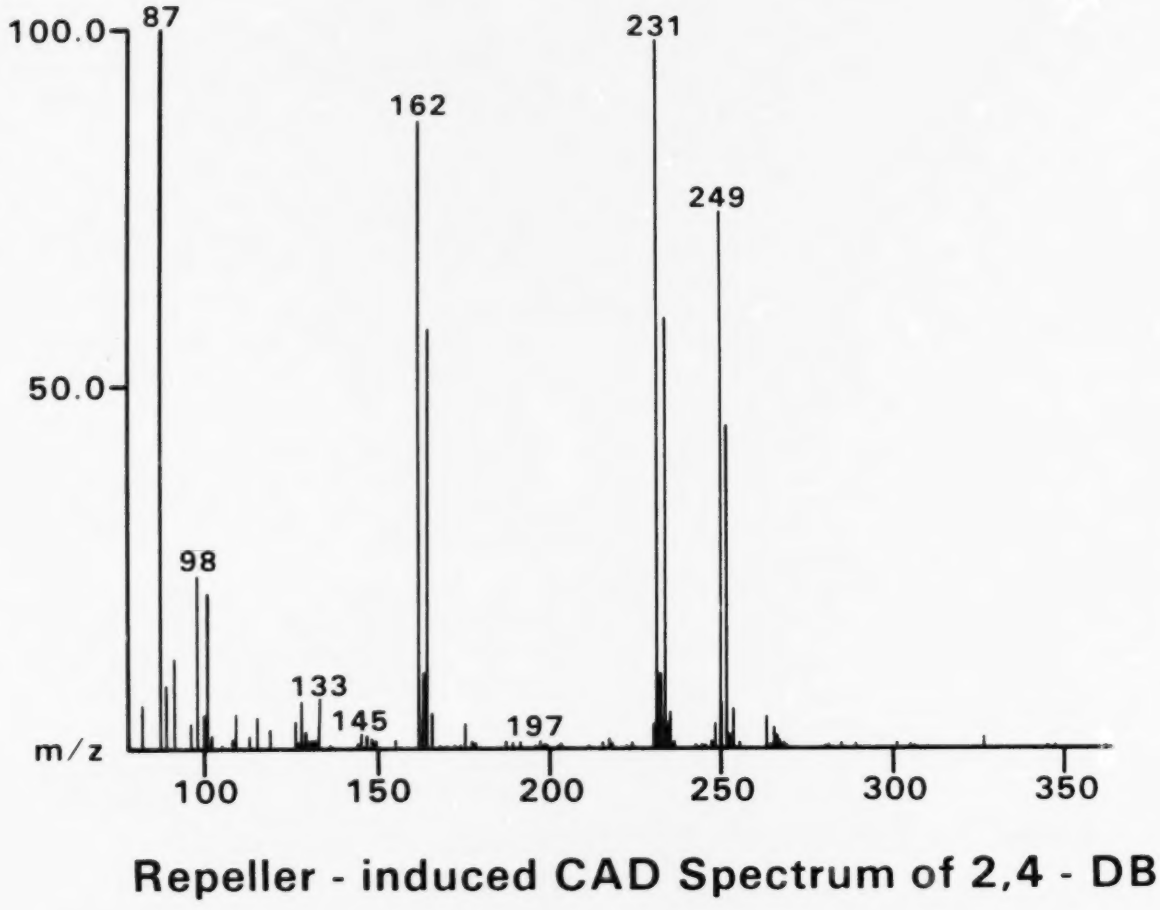


Figure 11. Repeller-induced CAD spectrum of 2,4-DB.

TABLE 9. POSITIVE ION THERMOSPRAY REPELLER-INDUCED CAD SPECTRA OF CHLORINATED ACID HERBICIDES

Compound	MW	Mass Spectra (% Relative Abundance)
Dicamba	220	$(M+H)^+$(69), M^+(19), $(MH-H_2O)^+$(100), $(MH-H_2O-CH_3)^+$(34), $(MH-OCH_3-OH)^+$ (27), $(C_6H_2Cl_2O)^+$(29), $(MH-H_2O-CH_3-Cl)^+$(21), $(C_6H_2Cl)^+$(22)
2,4-D	220	$(M+H)^+$(67), $(M+NH_4)^+$(7), $(MH+CH_3OH)^+$(5), $(M-COOH)^+$(42), $(MH-CH_2COOH)^+$(100), $(M-OCH_2COOH)^+$(22), $(MH-H_2O-Cl)^+$(17), 109(70)
MCPA	200	$(M+H)^+$(100), $(MH+CH_3OH)^+$(22), $(MH-H_2O)^+$(16), $(MH-HCOOH)^+$(99), $(MH-CH_2COOH)^+$(17), $(C_6H_3CH_3ClO)^+$(51), $(C_6H_3CH_3Cl)^+$(51), 89(90), 90(23)
Dichlorprop	234	$(M+H)^+$(56), $(MH+CH_3OH)^+$(12), M^+(19), $(MH-HCOOH)^+$(100), $(MH-CH_3CHCOOH)^+$(84), 109(20)
MCPP	214	$(M+H)^+$(48), $(MH+CH_3OH)^+$(9), $(MH-HCOOH)^+$(100), $(MH-CH_3CHCOOH)^+$(38), $(C_6H_3CH_3ClO)^+$(21), $(C_6H_3CH_3Cl)^+$(33), $(OCH(CH_3)COOH)^+$(30)
2,4,5-T	254	$(M+H)^+$ (50)$^+$, M^+(26), $(MH+CH_3OH)^+$(10), $(MH-HCOOH)^+$(44), $(MH-CH_2COOH)^+$(100), $(C_6H_2Cl_3)^+$(15), $(MH-CH_2COOH-COH)^+$(15), 145(21), 146(45), 133(35), 109(44)
2,4,5-TP	268	$(M+H)^+$(30), $(MH+CH_3OH)$(6), M^+(17), $(MH-HCOOH)^+$(60), $(MH-CH_3CHCOOH)^+$(100), $(MH-HCl-COOH)^+$(15), 159(23), 162(19)
2,4-DB	248	$(M+H)^+$(75), $(MH-H_2O)^+$(100), $(MH-(CH_2)_3COOH)^+$(88), 101(22), $((CH_2)_3COOH)^+$(100)
Dinoseb	240	$(M+H)^+$(100), $(MH-OH)^+$(11), $(MH-30)^+$(46), $(MH-NO_2)^+$(15), $(MH-2HNO_2)$(15), $(MH-2NO_2-C_2H_6)^+$(19), $(C_6H_2OH)^+$(20), $(C_6OH)^+$(18)

TABLE 10. COMPARISON OF METHOD DETECTION LIMITS:
METHOD 8150 vs. THERMOSPRAY HPLC/MS

Compound	Method 8150 MDL (µg/L)	Thermospray HPLC/MS MDL (µg/L)	(Ionization mode)
Dalapon	5.8	1.1	(-)
Dicamba	0.27	0.30	(-)
2,4-D	1.2	0.29	(+)
MCPA	249	2.8	(-)
Dichlorprop	0.65	0.27	(+)
MCPP	192	0.50	(+)
2,4,5-T	0.20	0.65	(-)
2,4,5-TP	0.17	4.3	(-)
Dinoseb	1.9	1.9	(-)
2,4-DB	0.91	0.34	(+)

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